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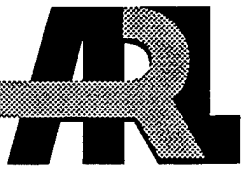

Influence of Temperature on the Distribution of Oxygen in Germanium Grown on Gallium Arsenide

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Kenneth A. Jones and Lawrence C. West

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The Fourier Transform infrared (FTIR) absorption spectrum from 500 to 4000 cm^{-1} was measured for several Ge films deposited on GaAs using ultra high vacuum (UHV) E-beam deposition at substrate temperatures ranging from room temperature (RT) to 500°C. The spectra indicate oxygen incorporation at low deposition temperatures whether or not the native oxide was removed from the substrate prior to film deposition. Previously, transmission electron microscopy (TEM) has shown that all of the Ge films on GaAs (100) at room temperature and those deposited at 100°C on GaAs (100) having a native oxide are amorphous, while those deposited at 100°C on oxide free (100) GaAs are crystalline, but highly defective. Secondary ion mass spectroscopy (SIMS) measurements show that the films deposited at RT contain more than two orders of magnitude more oxygen than the films deposited at 100°C or a single crystal film deposited at 400°C. $^{16}O/^{18}O$ diffusion studies definitively show that the excess oxygen in the films percolates in from the atmosphere. SIMS studies further reveal that thermally removing the GaAs substrate surface oxide or deposing a 1200A polycrystalline Au film on top of the Ge film has little effect on the incorporation of oxygen.

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CONTENTS

FIGURES

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Abstract

The Fourier Transform Infrared (FTIR) absorption spectrum from 500 to 4000 cm^{-1} was measured for several Ge films deposited on GaAs using ultra high vacuum (UHV) E-beam deposition at substrate temperatures ranging from room temperature (RT) to 500°C. The spectra indicate oxygen incorporation at low deposition temperatures whether or not the native oxide was removed from the substrate prior to film deposition. Previously, transmission electron microscopy (TEM) has shown that all of the Ge films deposited on GaAs (100) at room temperature and those deposited at 100°C on GaAs (100) having a native oxide are amorphous while those deposited at 100°C on oxide free (100) GaAs are crystalline, but highly defective. Secondary ion mass spectroscopy (SIMS) measurements show that the films deposited at RT contain more than two orders of magnitude more oxygen than the films deposited at 100°C or a single crystal film deposited at 400°C. $^{16}O/^{18}O$ diffusion studies definitively show that the excess oxygen in the films percolates in from the atmosphere. SIMS studies further reveal that thermally removing the GaAs substrate surface oxide or depositing a 1200Å polycrystalline Au film on top of the Ge film has little effect on the incorporation of oxygen.

Introduction

Ge is an attractive waveguide material[1] for GaAs based electro-optic integrated circuit devices utilizing mid infrared light (λ = 3 to 10 μm). Pure Ge is transparent at these wavelengths, has a relatively large index of refraction (n = 4.0) enabling it to better confine light via total internal reflection[1], and is essentially lattice matched to GaAs. This last condition enables one to heteroepitaxially grow Ge on GaAs that is of high crystalline quality. However, to achieve defect free epitaxy, one must deposit the Ge film at temperatures greater than 400°C[2]. At these temperatures, Ga and/or As diffuse across the interface and dope the Ge. The resulting carriers absorb a considerable amount of 10 μm light rendering the Ge unusable as a waveguide material[3,4]. The dopant concentrations can be reduced by lowering the growth temperature to 50°C or less, where virtually no free carrier absorption is measured. However, when the growth temperature is lowered to 50°C or (RT), a narrow absorption peak appears at 830 cm^{-1} simultaneously with a broad absorption peak from 2700 to 3700 cm^{-1}. These absorption features are due to a bulk effect in the Ge, because the peak height is reduced proportionately when the Ge film thickness is reduced by etching[3].

The observation that there is a Ge-O absorption peak[4,5] at 830 cm^{-1} indicates that the films grown at RT and 50°C are contaminated with oxygen. Initially, it was difficult to explain the origin of the oxygen because the Ge films were grown under ultra-high vacuum (UHV) conditions. Further, the absorption peaks were equally large for the films grown on oxide-free GaAs substrates as they were for films grown on GaAs with a native oxide. This strongly suggests that the substrate oxides were not the source of the oxygen contamination. In a somewhat analogous study, Foti et al.[6] found that silicon films deposited at RT were amorphous, and that oxygen percolated into them from the atmosphere. Double crystal x-ray diffraction spectra, for all of the films deposited at RT or 50°C and for those deposited at 100°C on an oxidized substrate, have no diffraction peaks. Therefore, these films are probably amorphous. This agrees with previous cross sectional TEM studies of Ge films deposited on (100) GaAs. While Ge films deposited on clean GaAs (100) at 400°C are single crystal epitaxially grown films[2], Ge films grown at RT are amorphous[7]. Ge grown at 100°C on GaAs (100) with a native oxide is also amorphous.

However, when Ge films are deposited at 100°C on oxide-free GaAs, they show good epitaxy with the GaAs out to about 60 nm where they become disordered, containing a high density of twins and stacking faults (>10^{11} cm^{-2}). The change to the more defective structure is likely due to three dimensional nucleation on the growing surface caused by the relatively low rate of surface diffusion at 100°C. This mechanism has been suggested by Eaglesham and Cerullo for the low temperature growth of Ge on (100) Si[8]. These authors also noted that at about 170°C there was a large increase in the thickness of the epitaxial layer, and they attributed it to the solid phase epitaxy of Ge[9]. This transition temperature should be lower for Ge growth on GaAs where lattice match is better and therefore the stress[10] is less. It is, therefore, not surprising that epitaxial growth is observed at 100°C.

The oxygen content in the Ge films was determined using secondary ion mass spectroscopy (SIMS). The films investigated were deposited on a GaAs substrate with and without a surface oxide at RT and 100°C, and at 400°C without an oxide. Some of the RT films also had a Au layer deposited in situ on top of Ge to determine if it could act as an effective diffusion barrier to the oxygen from the atmosphere. In addition, a film deposited at RT on an oxidized substrate was characterized, after it had been exposed in the load lock to a 50:50 mixture of $^{16}O/^{18}O$ for 24 hours, to confirm that the oxygen comes from the atmosphere. FTIR absorption spectra were obtained to determine how growth conditions affected the IR absorption, particularly the absorption associated with oxygen and free carriers.

Experiment

After loading the GaAs (100) wafers into a UHV E-beam evaporation system, they were heated to 600°C for 15 min to remove the surface oxide in situ and then cooled to the growth temperature, or they were directly heated to the growth temperature.

The Ge was deposited at about 1 Å/sec to a thickness of about 0.2 to 2.0 μm. For the samples with the Au diffusion barrier, the 1200Å of Au was deposited at about the same rate as the Ge. One sample was left in the load lock where it was exposed to a 50:50 mixture of $^{16}O/^{18}O$ for 24 hours, and the other samples were allowed to sit in an unenriched atmosphere. SIMS depth profiles for a number of samples were obtained using Cs^+ ion beam sputtering with negative secondary monitoring.

The FTIR absorption spectra of the films were recorded using the method described previously[4].

Results

The SIMS profiles (Fig. 1) of the films deposited at RT show that they do indeed contain large amounts of oxygen. Figures 1(a) and 1(b) are depth profiles of Ge films deposited on GaAs which is clean or which has a native oxide, respectively. Since these two films have essentially identical oxygen concentrations, one can conclude that the oxygen concentration in the Ge films is not affected by the presence or absence of a native oxide on the substrate (~100Å). Subsequent Auger analysis has determined the oxygen concentration in the RT Ge films to be ~0.5%. A 1200Å, polycrystalline Au capping layer results in somewhat lower oxygen levels (Fig. 1(c)). However, exposure to ^{18}O enriched oxygen results in ^{18}O inclusion throughout the Ge film in spite of a Au capping layer (Fig. 1(d)). This clearly shows that oxygen percolates into the Ge film from the atmosphere, and that the Au layer is not an effective diffusion barrier. The Au has too many grain boundaries, and/or has too many pores. Additional SIMS profiles (Fig. 2), show that the oxygen content in the Ge films grown at 100°C and 400°C is more than two orders of magnitude lower than those deposited at RT (Fig. 1). This reduced oxygen level is observed in all three profiles displayed in Fig. 2 even though Fig. 2(a), 2(b), and 2(c) are of polycrystalline, amorphous, and single crystal Ge films, respectively. Evidently, it is not necessary for a film to be crystalline to resist oxygen incorporation. Apparently, growth at 100°C or higher provides sufficient surface mobility to reduce the number of pores in the film below a critical value. Alternately, the increased mobility may be reducing the number of oxygen binding sites by increasing the number of Ge nearest neighbors.

The FTIR absorption spectra of the Ge films deposited on GaAs at RT and 100°C with substrate oxidation, and at 100°C without substrate oxidation are shown in Fig. 3. The Ge deposited at RT without oxides on the GaAs surface reveals strong oxide related absorption features including the absorption peak at 830 cm^{-1}. In all samples tested, bulk oxide related absorption features were perfectly correlated with the SIMS observation of high oxygen count rates throughout the Ge films. The absorption spectrum of the Ge deposited at 100°C without oxides on the GaAs surface shows increasing

absorption with increasing wavelength which is characteristic of free carrier absorption. The 100°C growth on an oxidized substrate exhibited none of the oxide related absorption features, as well as no indication of free carrier absorption. Therefore, the substrate's native oxide is an effective barrier to Ga, As, and Ge interdiffusion at 100°C while the 100°C growth temperature is sufficient to prevent the defects that result in oxidation of the Ge film.

Conclusions

The above experiments clearly show that oxygen is absorbed into RT grown Ge films. This suggests that the RT Ge films are more accessible to the oxygen (pores) or have more oxygen binding sites (dangling bonds) than the films deposited at 100°C. The SIMS data support these possibilities as the oxygen to Ge ion count ratio in RT grown Ge is ~1-20 while it is ~0.05 for the Ge films grown at 100°C. In addition, a GaAs oxidation layer has been shown to be an effective barrier to Ga and As diffusion into the Ge films grown at 100°C. As a result, of the growth conditions investigated, growing Ge at 100°C on an oxidized GaAs substrate results in the best waveguide material.

Acknowledgments

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References

1. A.D. Chaudhari, L.C. West, C.W. Roberts and L. Yu, IEEE Phot. Tech. Lett. 7 526 (1995).

2. M. Dubey, K.A. Jones, D.W. Eckart, L.M. Casas, and R.L. Pfeffer, Appl. Phys. Lett. 64, 2697 (1994).

3. M. Dubey, K.A. Jones, L.C. West, C.W. Roberts, J.P. Dunkel, L. Peticolas, and J.C. Bean, to be published in J. Appl. Phys. (May 1996)

4. M. Dubey, G.F. McLane, K.A. Jones, R.T. Lareau, D.W. Eckart, W.Y. Han, C. Roberts, J. Dunkel, and L. West, Mat. Res. Soc. Symp. Proc., 340, 411 (1994).

5. K.H. Beckman, Surf. Sci. 5, 187 (1966).

6. G. Foti, J.C. Bean, J.M. Poate, and C.W. Magee, Appl. Phys. Lett. 36, 840 (1980).

7. M. Dubey, R.T. Lareau, M.W. Cole, and K.A. Jones, "The Absorption of Light Due to Onygen in Ge Waveguides Grown on GaAs" (Poster presented at Mat. Res. Soc. Symp., San Fransico, California, 20 April 1995).

8. D.J. Eaglesham and M. Cerullo, Appl. Phys. Lett. 58, 2276 (1991).

9. L. Csepregi, R.P. Cullen, J.W. Mayer, and T. Sigmon, Solid State Commun. 21, 1019 (1977).

10. J. Aarts, W.M. Gerits, and P.K. Larsen, Appl. Phys. Lett. 58, 2278 (1986).

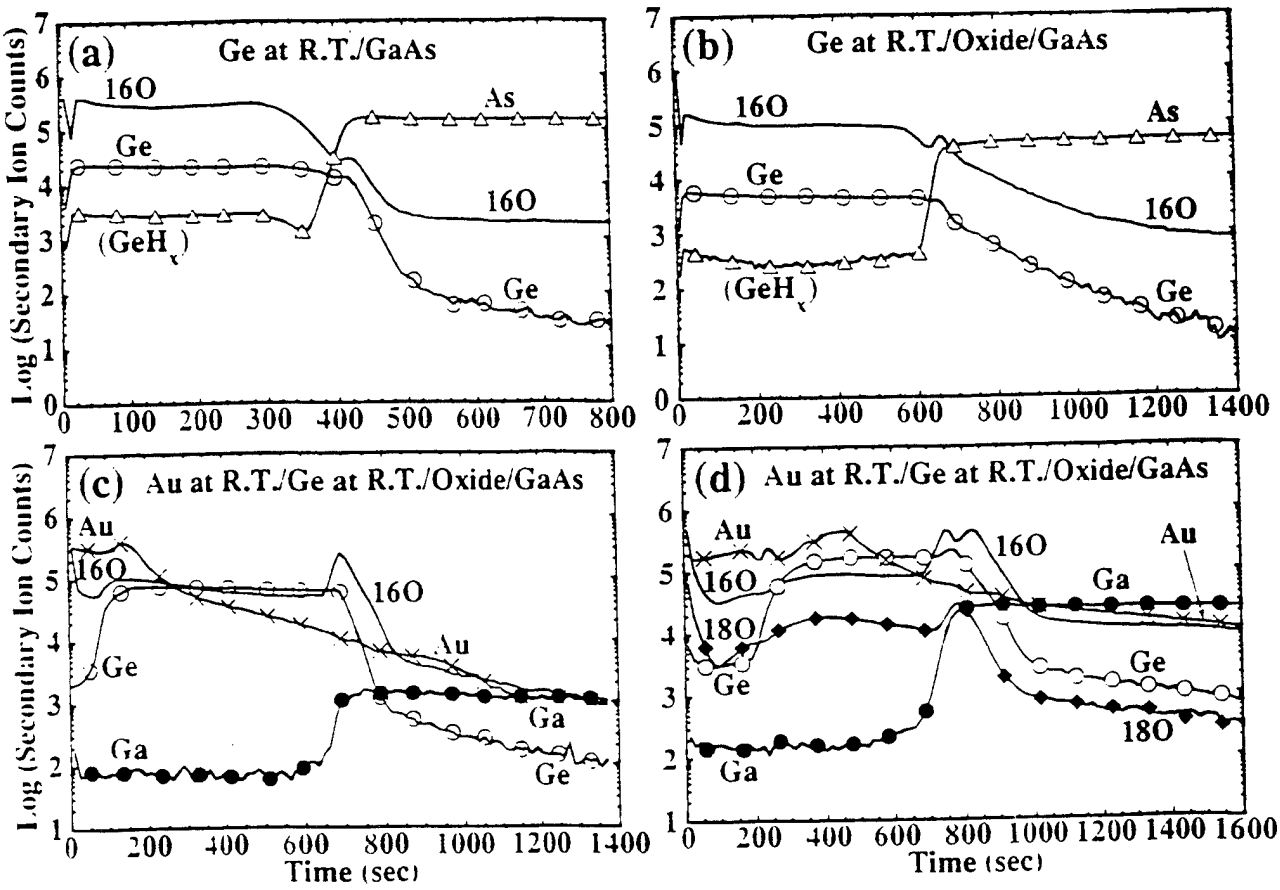

Figure 1. SIMS depth profiles of Ge films deposited on (100) GaAs at RT with (a) the substrate oxide thermally removed, (b) the substrate oxide left on, (c) a 1200 Å Au film deposited on the Ge film in situ, and (d) the Ge film exposed to an $^{16}O/^{18}O$ atmosphere in the UHV system load lock.

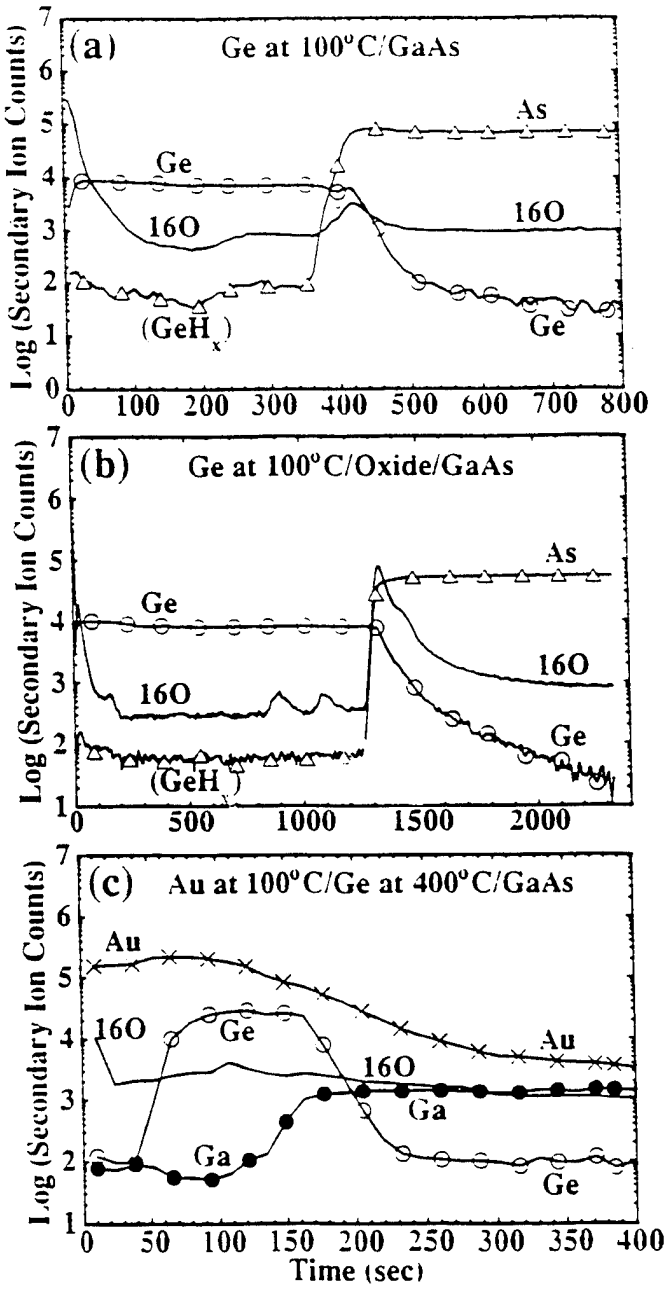

Figure 2. SIMS depth profiles of Ge films deposited on (100) GaAs at (a) 100°C with the substrate oxides thermally removed, (b) at 100°C with the oxides left on, and (c) at 400°C.

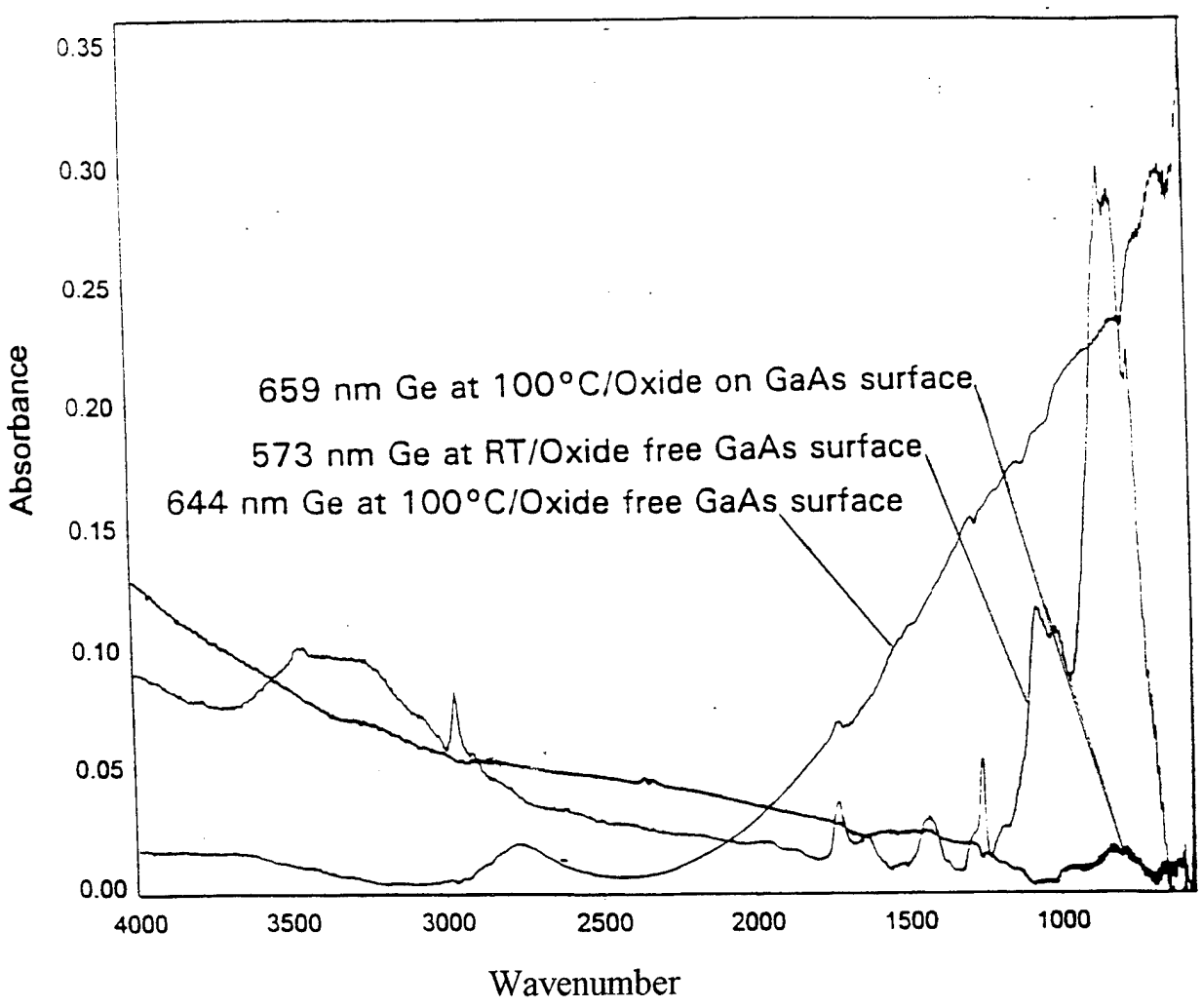

Figure 3. Multipass FTIR absorption spectrum of Ge films deposited at different temperatures.

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